Thickness dependence of the atomic and electronic structures of TiO$_2$ rutile (110) slabs and the effects on the electronic and magnetic properties of supported clusters of Pd and Rh.

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Using first principles calculations with ultrasoft pseudopotentials, we study the thick dependence of the atomic and electronic structures of (110) slabs of TiO$_2$ rutile having one to five layers. Thin slabs with an even and odd number of layers show significantly different structural characteristics and electronic properties that can affect photocatalysis as well as the catalytic behavior of supported clusters. We discuss the origin of the oscillating band gap for both an even and odd number of layers and the effects on the atomic, electronic, and magnetic properties of octahedral $M_6$ and icosahedral $M_{13}$ ($M=$Pd,Rh) clusters deposited on stoichiometric slabs with two and three layers. Calculations have also been carried out for a Pd atom deposited on different sites of a two layer slab. These results show that the bridging oxygen atoms are most reactive and preferred for adsorption. The adsorption energy of a Pd atom on the bridging site has only a weak dependence on the thickness of the slab. However, the adsorption energy of a cluster supported on a three-layer slab is significantly higher than the value for a two-layer slab due to significant structural differences and this alters the magnetic and electronic properties of the supported clusters. The magnetic moments of Pd clusters are reduced significantly higher than the value for a two-layer slab due to significant structural differences and this alters the magnetic and electronic properties of the supported clusters. The magnetic moments of Pd clusters are reduced after interaction with the support. However, for Rh clusters there is an increase in the magnetic moment. In general we find that the cluster-support interactions affect mainly the cluster and support atoms that are in contact at the interface. The variation in the band gap with slab thickness can, however, lead to metallic character of the slab after cluster adsorption and this could have important consequences for catalysis.

I. INTRODUCTION

TiO$_2$ rutile has wide applications in catalysis, photocatalysis, sensors, and composite materials. Its (110) surface is commonly used to study the catalytic behavior of supported clusters. Recently the interaction of water on (110) surface of TiO$_2$ has been studied to understand water/metal oxide interfaces and the charge transfer dynamics at the interface. Several ab initio calculations have been done on (110) slabs of TiO$_2$ rutile to model the surface behavior. An interesting result of these studies is the even-odd oscillations in the band gap as well as structural changes when the number of layers ($nL$) is varied. Bredow et al. studied the variation in the electronic properties of slabs by changing the thickness and suggested the origin of band gap oscillations to be due to surface-induced hybridization of Ti 3$d$ and O 2$p$ orbitals among the layers that affects significantly the bottom of the conduction band (CB). Therefore, proper consideration of the structural changes on the surfaces of the slabs is very important and as we shall show these are very significant. The changes in the electronic structure of slabs with a change in thickness could have important consequences for the catalytic behavior of supported metal clusters and could offer an interesting way to design catalysts as it has also been demonstrated recently from the catalytic activity of layers of TiO$_2$ on Mo(112) surface. Here we present results of ab initio calculations on the atomic, electronic, and magnetic properties of Pd and Rh clusters supported on thin TiO$_2$ (110) slabs with full atomic optimizations and explain the variation in the properties as $nL$ in the slab is changed.

The atomic relaxations on the stoichiometric (110) surface of TiO$_2$ rutile have been studied by many researchers. Ramamoorthy et al. have studied slabs having up to 6$L$ using the local density approximation (LDA) and ultrasoft pseudopotential method. They obtained an oscillatory convergence of the surface energy with different trends in the case of even and odd $nL$. Significant ionic relaxations were also found but the details were given only in the case of 5$L$. As we shall show, the ionic relaxations for even and odd $nL$ are quite different. Lindan et al. have done a similar study using a 3$L$ slab within generalized gradient approximation (GGA) and norm-conserving pseudopotential method. Though their results of ionic relaxations are similar to those obtained by Ramamoorthy et al., their convergence criteria for energy and forces are poor. Bates et al. have studied slabs having up to 7$L$ and compared results obtained from LDA and GGA. The surface energy was estimated to converge within 0.015 Jm$^{-2}$ for a slab with 6$L$. The GGA value was lower than the one obtained from LDA. Harrison et al. have studied a 7$L$ slab and showed that the large discrepancy between the calculated relaxation of the bridging oxygen and the measured value by Carlton et al. was due to temperature affects. The ionic relaxations have a general trend that undercoordinated ions (bridging oxygen, O($b$) and fivefold coordinated Ti, Ti(5$c$) in Fig. 1) relax inwards the unrelaxed surface while the surface Ti and O ions to be referred to as Ti(6$c$) and O($p$) with the same coordination as in bulk tend to relax outwards of the unrelaxed surface. The values of...
laxations on clean surfaces as well as for the cases when clusters are adsorbed. In the present work we have done such a study on slabs with different \(nL\) and by considering absorption of Pd and Rh clusters.

Clusters of transition metals such as Pd and Rh are important catalysts and their atomic and electronic structures have been widely studied.\(^{11,12}\) Both these metals are nonmagnetic in bulk. However, their clusters acquire magnetic moments. It is of interest to understand the modifications in the magnetic and electronic properties of the clusters after adsorption as well as the changes induced in the atomic and electronic structures of the oxide support for further understanding of reactions.\(^{13}\) Except for a few cases, the magnetic characterization of small supported clusters is still lacking because such calculations are computationally very demanding.

Moseler \textit{et al.}\(^{14}\) studied Pd\(_{1\times}\) clusters with \(N=2\)–7 and 13 on a MgO surface with an oxygen vacancy using a cluster model. The magnetic moments were shown to get quenched for \(N\leq3\) and reduced for \(N=13\). Also studies\(^{15}\) of Co\(_4\) and Ni\(_4\) clusters on MgO(001) surface with a cluster model showed the magnetic moments of the atoms in contact with the surface to be partially quenched. Bredow and Pacchioni\(^{16}\) have studied adsorption of Pd atoms on (110) surface of TiO\(_2\) rutile using a cluster model. They found that at low coverage a Pd atom bridges the protruding oxygen atoms on the surface while at higher coverage adsorption on surface Ti sites becomes preferable. However, no magnetic effects were considered in this study. We consider Pd and Rh clusters with 6 and 13 atoms soft landed on TiO\(_2\) (110) surface and report the modifications in the atomic, electronic, and magnetic properties of the clusters as well as the support due to cluster-support interaction. As a reference, calculations have also been done for adsorption of a Pd atom on TiO\(_2\) (110) slabs with different \(nL\). A preliminary report for supported Pd clusters was published in Ref. 17. There are further possibilities of different arrangements of cluster atoms on the substrate depending on the way clusters will be deposited. Also other possible adsorption configurations of the clusters may exist. These details have not been considered here.

The paper is organized as follows. In Sec. II we present our calculational method and in Sec. III results and discussion are given. Section IV gives a summary of our work.

\section*{II. COMPUTATIONAL METHOD}

The calculations have been performed using \textit{ab initio} ultrasoft pseudopotential formalism\(^{18}\) on (110) slabs of TiO\(_2\) rutile with 1L to 5L. The surface area of the unit cells of these slabs is fixed from calculated bulk lattice parameters.\(^{19}\) Further, keeping in view the supported clusters, a \(4c \times 2/\sqrt{2}a\) unit cell is used for all slab calculations. This leads to at least 8 Å separation between the clusters along the \(x\) and \(y\) directions (\(z\) axis being perpendicular to the surface). The slabs are separated by a vacuum layer of 10–12 Å which is sufficient to keep interaction between the slabs negligible\(^{1}\) even after deposition of clusters. The clusters are placed approximately 3 Å above the Ti(5c) atom in the channel on the surface layer. We considered three orientations of clusters with a face, edge, or vertex touching the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{(Color) (a)–(e) show projections along the \(x\)-axis of the relaxed geometries of (110) slabs of TiO\(_2\) rutile with 1L to 5L. The bridging (b) and planar (p) oxygen atoms as well as five and six coordinated Ti atoms are selectively marked as O(b), O(p), Ti(5c), and Ti(6c), respectively while for 1L, titanium atom with coordination four is marked as Ti(4c). Green (Red) balls represent Ti (O) atoms. The atomic structures of slabs with odd (even) layers have similar features. It can be noted that for 5L the dominant relaxations are in the surface layers.}
\end{figure}
surface. The orientation in which a face is in contact with the surface was found\cite{ref} to be most favorable for Pd8 while an edge is most favorable for Pd13. Furthermore, we considered slabs with different

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
# L & Ti(6c) & Ti(5c) & Bond distance (Å) & Gap (eV) \\
\hline
2 & 0.21 & -0.39 & 1.98 & 1.80 & 2.29 \\
3 & 0.03 & -0.30 & 1.95 & 1.86 & 1.27 \\
4 & 0.13 & -0.37 & 1.97 & 1.82 & 2.02 \\
5 & 0.04 & -0.34 & 1.96 & 1.83 & 1.58 \\
\hline
\end{tabular}
\caption{The displacements of Ti(6c) and Ti(5c) atoms along the z-axis with respect to the O(p) atom in the surface layer, bond distance Ti(5c)-O(p) along the surface and the z-axis, and the energy gap for different nL in the slab.}
\end{table}

other cases Table I shows the results of the displacements of Ti(5c) and Ti(6c) atoms along the z-axis with respect to the O(p) atoms in the outer layers and the Ti(5c)-O(p) bond distances in the optimized structures. These results are also shown in Fig. 2. The O(p) atoms on the surface move out as compared to the unrelaxed surface. As an example, in the case of 3L, the separation between O(p) atoms in the two outer layers is 6.91 Å compared with 6.57 Å in the unrelaxed case. This is comparable to the 0.22 Å increase in the O(p)-O(p) separation obtained by Lindan et al.\cite{ref} Also in the case of 5L, the separation between the corresponding outer O(p) atoms is 13.50 Å which means that it is elongated by 0.36 Å as compared to an unrelaxed slab. Therefore, comparing the 3L and 5L cases, the change in the relaxation is small and it is mostly confined in the two outermost layers as

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Oscillations in (a) the band gap, the displacement of (b) Ti(6c) and (c) Ti(5c) atoms with respect to the O(p) atom in the surface and (d) the Ti(5c)-O(p) bond length along the z-axis, as the number of layers (nL) in the slab is changed. In (a) solid (dotted) curve shows our (Ref. 4) results while the horizontal lines are the corresponding calculated values for the bulk. In (b)–(d) the dotted horizontal line shows the experimental values for a bulk truncated surface (Ref. 7). There are large error bars in the experimental values which have not been shown. The opposite behavior of the convergence to asymptotic limit for even and odd nL can be noticed.}
\end{figure}
it can be seen also in Fig. 1. The O(b) and Ti(5c) atoms are displaced inwards the surface while the Ti(6c) atoms move outwards of the surface, in agreement with earlier studies.\textsuperscript{6,9} In both the cases of 3L and 5L, the Ti(6c)-O(b) bond length is nearly the same (1.85 Å). Therefore, this bond length is not very sensitive to \( n \)L except for the case of 1L. Similarly the Ti(5c)-O(p) bond length on the surface has small variation with \( n \)L (1.95 and 1.96 Å for 3L and 5L, respectively). However, the Ti(5c)-O(p) bond length along the \( z \)-axis changes more significantly with \( n \)L (Table I and Fig. 2). For 3L case it is 1.86 Å while for 5L this is 1.83 Å. The corresponding experimental values on a bulk terminated surface are 1.71±0.07 Å, 1.84±0.05 Å, and 1.84±0.13 Å\textsuperscript{7} for Ti(6c)-O(b), Ti(5c)-O(p) (surface), and Ti(5c)-O(p) (\( z \)-axis), respectively. The calculated trends of the bond length changes are in agreement with the values obtained from experiments and earlier calculations.

For the case of even \( n \)L, the Ti(5c) and Ti(6c) atoms in the two outer layers are on top of each other and their relaxations are in the same direction. This is in contrast to odd \( n \)L in which case Ti(6c) and Ti(5c) atoms in one outer layer are on top of the Ti(6c) and Ti(5c) atoms in the other outer layer, respectively, and their displacements are in opposite directions with respect to the central layer. This leads to larger inward relaxation of Ti(5c) as well as larger outward relaxation of Ti(6c) atoms in slabs with even \( n \)L (Fig. 2). The convergence of relaxation and bond lengths with increasing even and odd \( n \)L shows opposite trends. As an example the outward relaxation of Ti(6c) atoms decreases with increasing thickness of the slab for even \( n \)L but it increases for odd \( n \)L as also shown in Fig. 2(b). The asymptotic behavior of our results for the relaxation is in good agreement with the experimental value on bulk terminated surface.\textsuperscript{7} Similarly the Ti(5c)-O(p) bond length along the \( z \)-axis tends to achieve the asymptotic behavior obtained experimentally on bulk terminated surface, but the extrapolation of our results tend to give a slightly shorter value [Fig. 2(d)] by 0.01 Å. As there is a large error bar of ±0.13 Å in the experimental value, this agreement can be considered to be very good. Our calculations give the displacement of Ti(5c) inwards the surface to be significantly larger [Fig. 2(c)] than the experimental value, though again there is an significant error bar in the experimental result. It is to be noted that the experimental value of the Ti(6c)-O(b) bond length is significantly shorter than obtained by us as well as in earlier calculations. Since our result for the relative displacement of Ti(6c) with respect to O(p) is in excellent agreement with experiment, we conclude that O(b) has a larger relaxation towards the surface than obtained from calculations. Similar result has been obtained by others as discussed by Harrison \textit{et al.}\textsuperscript{8} who have shown the reason of this discrepancy to be the large thermal motion of this oxygen atom even at room temperature due to a nearly flat energy surface. As we shall show later, the position of O(b) is also affected by adsorption of clusters. The significant discrepancy for the relaxation of Ti(5c) is therefore related to the large uncertainty of ±0.13 Å in Ti(5c)-O(p) bond length along the \( z \)-axis and thermal effects. In general the results shown in Table I and Fig. 2 suggest that slabs with \( n = 7 \) may achieve atomic relaxations close to the asymptotic values. A similar result was obtained by Bates \textit{et al.}\textsuperscript{3} These results also suggest that with an increase in \( n \), the behavior of even and odd \( n \)L slabs would tend to become similar as the inner layers would tend to become bulk like.

B. Electronic structures of slabs

The electronic density of states (DOS) of the slabs with different \( n \)L are shown in Fig. 3 together with the calculated bulk DOS. The latter shows a band gap of about 1.85 eV. The VB and CB are in general dominated by O-2\( p \) and Ti-3\( d \) states, respectively but there is some covalent bonding character also between Ti and O atoms. The electronic structure of 1\( L \) shows metallic behavior. However, for even \( n \)L the band gap becomes even larger than the bulk value while for odd \( n \)L it is smaller than the bulk value (Table I). Therefore, the gap oscillates as the number of layers is increased [Fig. 2(a)] similar to the results of Bredow \textit{et al.}\textsuperscript{4} However, our values of the band gap in all cases (2\( L \) to 5\( L \)) differ significantly from their values [Table I and Fig. 2(a)]. Their calculated difference between the band gaps of 2\( L \) and 4\( L \) slabs is 0.63 eV compared to our value of 0.27 eV. The convergence to the asymptotic value of the band gap is opposite for odd and even \( n \)L as it is also found in the case of the atomic relaxations and bond lengths. From Fig. 2(a) the value for \( n = 7 \) can be expected to be close to the bulk value. In Fig. 2(a) we have compared our results with those of Bredow \textit{et al.}\textsuperscript{4} and it can be seen that the convergence of our band gap to the asymptotic limit is better. These results are important for the proper modeling of the bulk surface.

The large difference in the band gap for even and odd \( n \)L comes from the fact that for odd \( n \)L some states at the bottom of the CB and VB shift down to lower energies. We refer to these states as surface states. In order to understand the
potential along the $z$ direction. This is more clearly seen from the orbital decomposed DOS for the Ti(5$c$) atoms [Fig. 4(c)] which show dominant contribution to the surface states from the $z^2$ orbital. As the number of layers in the slab increases, the effect on the central layer decreases as it can be seen in Fig. 4(d) for the case of 5L for which the splitting of the surface states from the rest of the band is reduced. Therefore, for a thick slab only the surface region is likely to show such states as one would also expect intuitively.

In order to understand the larger gaps for slabs with even $nL$ as well as the absence of the surface states, we find that the buckling of the layers leads to nearly the same separation between Ti(5$c$) and Ti(6$c$) atoms along the $z$-axis in successive layers as in the unrelaxed surface (3.28 Å). For example, in the case of 2L slab this value is 3.31 Å. However, for 3L slab this is 3.15 Å. Therefore, the relative effect of the surface on the inner layers is small for even $nL$ slabs and only small changes occur in the hybridization of the orbitals. However, for odd $nL$, the reduced separation along the $z$-axis affects the overlap of the Ti-$d_{z^2}$ orbitals which is reflected in the orbital decomposed DOS. This leads to the splitting of the surface states below the CB and VB in slabs with odd $nL$. On the other hand a small increase in the case of even $nL$ leads to small splitting of states above the VB. The bond length between the Ti(6$c$) surface atoms and O(b) atoms is reduced to 1.83 Å from the corresponding calculated bulk value of 1.94 Å and it is nearly independent of the thickness of the slab (Ti(6$c$)-O(b) bond distances for 2L–5L are 1.83, 1.85, 1.84, 1.85 Å, respectively). As discussed before, the bond length between Ti(5$c$) and the O(p) along the $z$-axis is also reduced (Table I) but it is more sensitive to the number of layers compared to the Ti(6$c$)-O(b) bond. For 3L slab this bond length is the longest (1.86 Å) and the Ti(5$c$)-O(p) bond length along the surface is also reduced to 1.95 Å as compared to 1.98 Å for the 2L slab. This reduced bond length leads to an increase in the covalent bonding between Ti(5$c$) and O(p) as it is seen in Fig. 4(b) for Ti(5$c$) and also from the DOS of $d_{xy}$ orbital in Fig. 4(c). Such an affect is reduced for the 5L slab. The charge density isosurface contours are similar to the results given by Bredow et al., and there is covalent bonding characters between Ti(5$c$) and O(p) atoms along the $z$-axis as well as Ti(6$c$) and O(b) atoms. For the 2L case the Ti(5$c$)-O(p) separation is lower (1.80 Å) than for the 3L case (1.86 Å). This results into stronger covalency for the 2L slab.

### C. Adsorption of a Pd atom

We carried out test calculations for a Pd atom adsorbed on different positions on a slab with 2L as shown in Fig. 5. It is found that the most favorable site for adsorption of a Pd atom is between the O(b) atoms. This is in agreement with the earlier work as well as the results on other metal atoms on this surface. In this configuration [Fig. 5(a)] the Pd-O(b) bond distance is quite small (2.14 Å) and also the Ti(6$c$)-Pd bond is well optimized (2.53 Å). Adsorption of a Pd atom on a hollow site [Fig. 5(b)] is unfavorable by only 0.1 eV. In this case the Pd atom interacts with Ti(5$c$), O(b) as well as O(p) atoms. The Ti(5$c$)-Pd, shortest O(b)-Pd, and
D. Supported Pd and Rh clusters

In order to understand the changes in the atomic and electronic structures as well as the slab thickness dependence of cluster properties, we considered Pd\(_N\) and Rh\(_N\) (\(N=6\) and 13) clusters supported on 2L and 3L slabs as representative for slabs with even and odd \(nL\). The thinner layers have been chosen due to the heavy calculations involved in studying magnetic properties of this system. Also as the changes in the atomic structure of the slab with increasing size are smaller, we expect our calculations to capture the most significant features of the cluster-surface interactions. Preliminary results for the orientation dependence of the interaction of Pd\(_6\) and Pd\(_{13}\) clusters on 2L slab were reported in Ref. 17. In this study octahedral Pd\(_6\) and icosahedral Pd\(_{13}\) were considered as these are the most stable structures of these clusters.\(^1\) The most favorable orientation for Pd\(_6\) cluster among the orientations considered in this study was found to be the one in which a face touches the surface while for Pd\(_{13}\) the orientation with an edge touching the surface has the lowest energy. We focus in the following on the understanding of the electronic structures in the cases of adsorption of Pd clusters on 2L and 3L as well as the clusters of Rh.

The free clusters of Pd\(_6\) and Pd\(_{13}\) have magnetic moment of 2 and 8 \(\mu_B\), respectively. The relaxed geometries of Pd\(_{13}\) cluster adsorbed on 2L and 3L slabs are shown in Fig. 6. It can be seen that the atomic structure of the free cluster is only slightly affected by the interaction with the support. In the case of the 2L slab, the interaction of the Pd\(_{13}\) cluster is predominantly with the O\((b)\) atoms. The Ti\((5c)\) atom interacts weakly because of the buckling of the surface and it is displaced upwards by 0.15 Å as compared to the position in the relaxed clean surface. However, for 3L slab, the interaction of Ti\((5c)\) atom with the cluster is significant and it is displaced upwards by 0.41 Å compared to the clean relaxed surface. Also the O\((b)\) atoms in the surface layer drift by 0.15 Å towards the cluster while other atoms have only a minor effect (Table II). These results suggest that the vibrational frequencies of the O\((b)\) and Ti\((5c)\) atoms should change very significantly after cluster adsorption and this could also be a good way to identify the adsorption position from experiments. Similar results have also been obtained for Pd\(_6\) cluster adsorbed on slabs with 2L and 3L and these are reported in Table II. However, in this case the size of the cluster is small and it can be accommodated in the channel more easily as shown in Fig. 6. This also leads to much shorter Pd-O\((p)\) bond lengths (2.12 Å) than the corresponding value of 2.87 Å for Pd\(_{13}\) cluster. This additional interaction leads to an increase in the adsorption energy of Pd\(_6\) cluster on both 2L and 3L slabs.

The adsorption energy of the cluster \((E_{ad})\) is calculated from

\[
E_{ad} = E_{\text{TiO}_2} + E_{M_N} - E_{\text{TiO}_2 + M_N}
\]

where \(E_{\text{TiO}_2}\), \(E_{\text{TiO}_2 + M_N}\), and \(E_{M_N}\) are the total energies of \(M_N\) cluster adsorbed on a 2L or 3L slab, clean 2L or 3L slab, and
TABLE II. The maximum atomic displacements of Ti(5c) and O(b) atoms towards the cluster, the closest bond distance between the cluster and the surface, adsorption energy \( (E_{ad}) \), and magnetic moment of adsorbed clusters.

<table>
<thead>
<tr>
<th>Layers</th>
<th>Clusters</th>
<th>Ti(5c)</th>
<th>O(b)</th>
<th>Ti(5c)-M</th>
<th>O(b)-M</th>
<th>O(p)-M</th>
<th>( E_{ad} ) (eV)</th>
<th>Moment (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Pd(_6)</td>
<td>0.05</td>
<td>0.07</td>
<td>2.82</td>
<td>2.16</td>
<td>2.12</td>
<td>2.18</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>Pd(_{13})</td>
<td>0.15</td>
<td>0.05</td>
<td>2.93</td>
<td>2.19</td>
<td>2.87</td>
<td>1.44</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>Pd(_6)</td>
<td>0.43</td>
<td>0.14</td>
<td>2.48</td>
<td>2.14</td>
<td>2.16</td>
<td>3.42</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>Pd(_{13})</td>
<td>0.41</td>
<td>0.15</td>
<td>2.54</td>
<td>2.13</td>
<td>2.79</td>
<td>2.69</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>Rh(_6)</td>
<td>0.36</td>
<td>0.15</td>
<td>2.51</td>
<td>2.02</td>
<td>2.15</td>
<td>4.89</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>Rh(_{13})</td>
<td>0.34</td>
<td>0.10</td>
<td>2.51</td>
<td>2.06</td>
<td>2.65</td>
<td>3.65</td>
<td>21.0</td>
</tr>
</tbody>
</table>

\( ^a \)Configurations and moments for free M=Pd and Rh clusters have been taken from Refs. 11 and 12, respectively.

The isolated \( M_N \) cluster. The adsorption energies for Pd\(_6\) and Pd\(_{13}\) clusters are given in Table II. The adsorption energy (2.69 eV) for Pd\(_{13}\) on 3L slab is significantly higher as compared to 1.44 eV for the 2L slab. A similar trend is obtained for supported Pd\(_6\) cluster. However, as discussed above, the adsorption energy of Pd\(_6\) is higher (Table II) for both 2L and 3L slabs. Compared with the binding energies of 1.92 and 2.29 eV/atom for the free Pd\(_6\) and Pd\(_{13}\) clusters,\(^1\) respectively, the adsorption energies for the clusters are relatively small and therefore the effects on the properties of the clusters are also weak and more local in nature.

The stronger interaction of the cluster with the 3L slab leads to a reduction in its magnetic moment. For Pd\(_{13}\) it reduces to about 6.5 \( \mu_B \) from the value of 8 \( \mu_B \) for the free cluster. However, the weaker interaction on 2L slab leaves the magnetic moment distribution on the cluster nearly unchanged. Quenching of the magnetic moment of supported Co\(_4\) cluster\(^1\) as well as Pd clusters\(^1\) on MgO surface has been reported. The reduction in the magnetic moments is around the ions in contact with the surface while the magnetic polarization is affected little around the ions away from the surface. There is a small polarization of opposite spin around the Ti(5c) ion while a small polarization of the same spin is induced around the O(b) ions as shown for Pd\(_{13}\) in Fig. 7. Similar calculations have been performed for octahedral Rh\(_6\) and icosahedral isomer of Rh\(_{13}\) adsorbed on a 3L slab. The results are given in Table II. In both these cases the bond lengths of Rh atoms in contact with the surface are generally shorter than in the case of Pd clusters and the adsorption energies are significantly higher. This is due to more \( d \) holes in the 4d band of Rh. Also similar to Pd\(_6\), the adsorption energy of Rh\(_6\) cluster is about 1.24 eV higher than the value for Rh\(_{13}\). Accordingly we can expect more significant changes in the properties of these clusters.

Figures 7(a) and 7(b) show the charge and spin-density isosurface contours for Pd\(_{13}\) on 2L and 3L slabs. For 3L slab the charge density shows that the strong interactions between the surface and the cluster originate predominantly from O(b) and Ti(5c) atoms. The bonding between the Ti(5c) atom and the Pd atoms is enhanced while the covalent bonding character between Ti(5c) and O(p) is reduced after adsorption of cluster on a 3L slab. However, for 2L slab the weaker interaction between Pd and Ti(5c) atoms is clearly seen. The decrease in the moments of Pd\(_{13}\) cluster can be attributed to contacts with Ti(5c) atoms. A comparison of the free and supported cluster states shows (Fig. 8) that a large fraction of the Pd 4d states fall within the band gap of TiO\(_2\) and some states get distributed over the whole band of the slab due to hybridization, though the main features in the DOS are very similar in the supported and free clusters. The total and partial DOS (Fig. 8) show that predominantly the O-2p states lie about 2 eV below the Fermi level and the Ti-3d states are above the Fermi level. Pd-4d states are located in between these states. The Pd-4d states have a few holes while the Ti-3d states are mostly unoccupied. The surface states for the 3L slab closely match with the electronic states of the Pd clusters [Fig. 8(b)]. A significant effect is that the interaction with the surface states at the bottom of the CB of the 3L slab depopulates some of the up-spin states and it results in the reduction of the magnetic moments. Also this leads to small occupancy of the surface states of the TiO\(_2\) slab as the Fermi level now lies in the surface states [Fig. 8(b)]. Accordingly the supported cluster slab attains metallic character. However, in the case of the 2L slab the surface states at the bottom of CB are not present [Fig. 8(a)] and the interaction between the cluster and the surface is weak. Fig. 8(a) shows that the Ti 3d states are not occupied.

For Rh\(_{13}\) free cluster there are a few up-spin states that are unoccupied [Fig. 8(c)]. However, after adsorption on TiO\(_2\) (110) surface these up-spin states get filled leading to an increase in the magnetic moment of 2 \( \mu_B \) (Table II). The charge and spin-polarization iso-surface contours are shown in Figs. 7(e) and 7(f), respectively. It is seen that the general trend of the interaction is similar to Pd clusters. The displacement of Ti(5c) atom is slightly reduced (Table II) for both Rh\(_6\) and Rh\(_{13}\) as compared to Pd clusters while for O(b) the upward displacement is enhanced for Rh\(_6\) but decreased for Rh\(_{13}\). The mean bond distance in Rh\(_{13}\) cluster is 0.1 Å shorter as compared to Pd\(_{13}\) cluster.\(^2\) Therefore, Rh\(_{13}\) cluster can come closer to the surface such that the cluster to surface atom bond lengths are reduced (see Table II) compared with Pd\(_{13}\). This also leads to an overall increase in the
interaction energy. Rh$_{13}$ cluster induces opposite spin-polarization around Ti(5c) ion and same spin-polarization around O(b) ions which is more significant [Fig. 7(f)] as compared to Pd$_{13}$ cluster. Also there is small opposite spin-polarization in Rh$_{13}$ cluster but the polarization around Rh ions is enhanced due to an increase in the magnetic moments. Similar behavior has been obtained for Rh$_6$. However, in this case there is more significant interaction with O(b) atoms and the Rh-O(b) bond length is reduced to 2.02 Å which is the shortest among all the cases we have studied (Table II). The interaction with O(p) atoms is also significant as Rh-O(p) bond length is 2.15 Å but this value is close to the one obtained for Pd$_6$. The DOS for Rh$_6$ adsorbed on 3L slab is shown in Fig. 8(d). It is seen that there is a significant change in the distribution of states near the Fermi energy. The Ti 3d unoccupied states at the bottom of CB overlap with the Rh$_6$ cluster states and get slightly occupied as also in the case of Rh$_{13}$. From Fig. 8(c), it can be seen that the occupancy of the Ti 3d states is increased for Rh$_{13}$ as compared to Pd$_{13}$ cluster.

From these results some interesting consequences for cluster adsorption as well as reactions can be drawn. First of all the band gap plays an important role in the reactivity of the clusters with the support as well as in the modifications of their properties. If the cluster states lie completely within the band gap, the interaction is generally weaker with little effects on the electronic structure. Secondly, the unoccupied states near the bottom of the CB of TiO$_2$ can be slightly occupied due to adsorption of clusters. This could induce metallicity in the surface layer and it can have important consequences for reactions. Also in such cases the interaction of the cluster with the surface is more significant. On TiO$_2$ surface this also depends on the cluster size as larger clusters cannot interact properly with atoms in the channel. Furthermore, for the same size of the clusters, the elements with a smaller size can interact better with the support. Finally we find a different behavior of magnetism for Pd and Rh clusters. Our calculations show that the magnetic moments of the clusters can be reduced as well as enhanced depending upon the system. As the interaction with oxygen atoms is generally favorable, there could be a possibility of the change in the shape of cluster to planar type under certain deposition conditions.

IV. SUMMARY

In summary we have studied the atomic and electronic structures of TiO$_2$ rutile (110) thin slabs with different number of layers using first principle calculations. The origin of buckling in the case of even number of layers as well as a decrease in the band gap of slabs with odd number of layers compared with bulk have been explained. The band gap differs from the bulk value significantly for such thin slabs. Therefore, such layers are interesting for designing photocatalysts. The differences in the properties of slabs with an odd and even number of layers affect significantly the interaction of clusters with the substrate, the magnetic moments and the electronic structures of clusters. The changes are, however, mostly for atoms of the cluster and the substrate in contact with each other and more significant for odd number of layers in the slab. In the latter case the band gap is reduced due to the presence of surface states that interact with the electronic states of the cluster. The surface states have dominant contribution from Ti atoms lying below the Ti(5c) atoms and, therefore, such an effect, though weaker, should also occur on the (110) surface of bulk TiO$_2$. The large deviations in the atomic and electronic structures of slabs with even and odd number of layers suggests that thin layers deposited on another material could be used to develop substrates of the same material with varying properties which may help in tailoring catalytic behavior. The reduced band gap and the development of metallicity can have important
consequences for catalysis as the TiO₂ surface may itself behave as catalyst. Our results give the general trends of the interaction of clusters with slabs having even and odd number of layers and to obtain the proper behavior for infinite surfaces, one may need to consider thicker slabs. For thicker slabs we can expect slightly weaker interaction of the clusters as compared to the case of odd nL because the band gap will increase with increasing n. Also even in the case that the cluster and the substrate states do not overlap, there is an interesting possibility that at high temperatures, electrons could be promoted to the conduction band of TiO₂ and this could affect the catalytic behavior. Our results also show that both enhancement as well as quenching of the magnetic moments of a cluster could occur after deposition on a substrate. It would be of interest to explore further the role of magnetism on reactions on supported clusters. A further interesting aspect of cluster deposition is the different atomic arrangement due to the interaction with the substrate and that could lead to very different properties of the metal clusters. Such studies remain the subject for further studies.

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The electronic and structural properties of bulk TiO$_2$ have been obtained from a $2 \times 2 \times 2$ supercell in tetragonal structure. The BZ of this supercell was sampled by Monkhorst-Pack mesh of $(4 \times 4 \times 6)$ $\mathbf{k}$-points. The ions and the cell size were optimized without any constraint. The calculated lattice parameters, $a = 4.66$ Å and $c = 2.98$ Å, agree well with the experimental values of 4.594 and 2.959 Å (Ref. 20) respectively. The optimized short and long Ti-O bond distances are 1.97 and 2.00 Å, respectively. The band gap of 1.85 eV is smaller than the experimental value of 3 eV due to the GGA (Ref. 21).

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